



The energies of non-standard intermolecular interactions are competitive with conventional hydrogen-bonding

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Research Centre for Crystalline Materials

AsCA 2018 CRYSTAL 32
December 2-5 2018 | Auckland, New Zealand



Crystals?

Why do crystals form?

How do crystals form?



Crystal Engineering

Determine how
Molecules pack

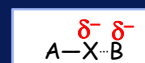
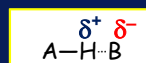
Design specific
architectures

Optimise for
applications

Intermolecular Interactions

Well known...

Hydrogen-bonding (HB)
Halogen-bonding (HB)



Intermolecular Interactions

Well known...

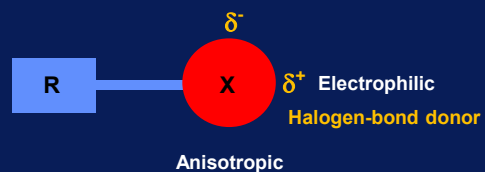
Hydrogen-bonding (HB)
Halogen-bonding (HB)

Odd Hassel
1897 – 1981



Halogen-bonding

Halogen-bond acceptor Nucleophilic



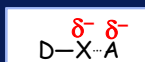
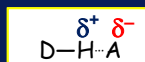
Polar cap, σ -hole

Intermolecular Interactions

Well known...

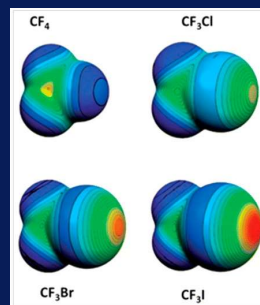
Hydrogen-bonding (HB)

Halogen-bonding (HB)



(HB)²: Similar in energy = 5 - 15 kcal/mol

σ -hole



Halogen-bonding

Chalcogen-bonding

Pnicogen-bonding

Tetrel-bonding

Aerogen-bonding

Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P.
Halogen Bonding: The Sigma-Hole *J. Mol. Model.* **2007**, *13*, 291–296

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Chemie

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A Journal of the
German
Chemical Society

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Aerogen Bonding Interaction: A New Supramolecular Force?*

Antonio Bauzá, Prof. Antonio Frontera

First published: 07 May 2015 | <https://doi-org.ezproxy.lancs.ac.uk/10.1002/anie.201502571>
| Cited by: 112

!

*This work was funded by the MINECO of Spain (CONSOLIDER-Ingenio 2010 project CSD2010-0065 FEDER funds).

...favorable noncovalent interaction between a covalently bonded atom of Group 18 (known as noble gases or aerogens) and a negative site, for example, a lone pair of a Lewis base or an anion.

Faraday Discussions

Cite this: *Faraday Discuss.*, 2017, 203, 93



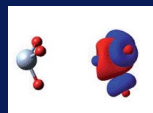
PAPER

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Intermolecular interactions in molecular crystals: what's in a name?

Alison J. Edwards, ^a Campbell F. Mackenzie, ^b
Peter R. Spackman, ^b Dylan Jayatilaka ^b and Mark A. Spackman ^{b*}



isosurfaces of the
deformation electron density

Issue 9, 2009

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Next Article



From the journal:
Chemical Society Reviews

How molecules stick together in organic crystals: weak intermolecular interactions

Jack D. Dunitz^{*a} and Angelo Gavezzotti^{*b}



...most organic molecules feature hydrogen atoms at the periphery and so that C–H...X interactions are inevitable

Chem. Soc. Rev., **2009**, *38*, 2622–2633



Prevalence of Space Group Adoption

CSD: 865,342 entries

<i>P2₁/c</i>	279041	34.5
<i>P1̄</i>	198014	24.7
<i>C2/c</i>	67434	8.4
<i>P2₁2₁2₁</i>	58438	7.2
<i>P2₁</i>	41791	5.2
<i>Pbca</i>	26951	3.3

Six close-packing SG's account for >83% of structures

How significant are non-covalent interactions: tetrel-bonding



DOI: 10.1002/chem.201804676

CHEMISTRY
A European Journal
Full Paper



■ Sn Interactions



S...Sn Tetrel Bonds in the Activation of Peroxisome Proliferator-Activated Receptors (PPARs) by Organotin Molecules

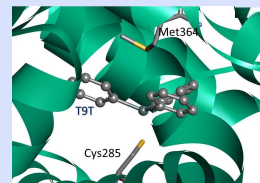
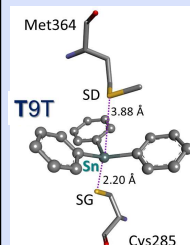
Antonio Frontera and Antonio Bauzá[✉]

Abstract: In this study, a PDB (Protein Data Bank) analysis and theoretical calculations (PBE0-D3/def2-TZVP level of theory) were combined to analyze the impact of S...Sn tetrel-bonding interactions in the activation mechanism of peroxisome proliferator-activated receptors (PPARs) by two organotin derivatives, triphenyltin (TPT) and tributyltin (TBT). The presence of a covalently bonded CYS285 to the organotin molecule was found to be key to enhance the σ-hole-donor ability of the tin atom, thus strengthening the tetrel-bonding interaction with a sulfur atom belonging to a vicinal methionine residue (MET364).

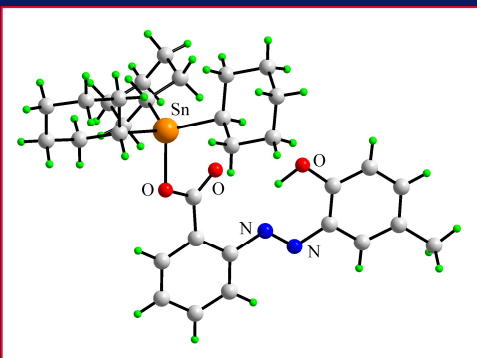
Chem. Eur. J. 2018, 24, 16582–16587

Tetrel-bonding in biology

pdb 3jw5
PPAR γ & T9T

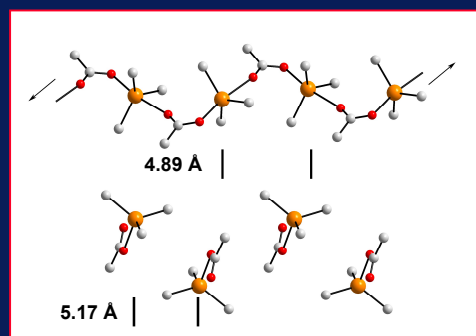
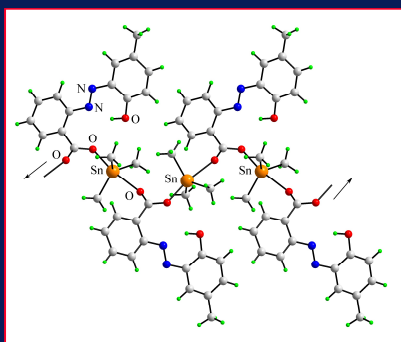


Ignaz Caracelli



Systematic analysis of $\text{R}_3\text{Sn}(\text{O}_2\text{CR}')$

R	^{117}Sn solution	^{117}Sn solid-state
Cy	-8.5	23.7
Me	24.7	148.1



Tetrel-bonding: energy

THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article
pubs.acs.org/JPCA

Systematic Elucidation of Factors That Influence the Strength of Tetrel Bonds

Steve Scheiner*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

DOI: 10.1021/jp402603g
J. Phys. Chem. A 2014, 118, 10264-10274

(HB)²: Similar in energy = 5 - 15 kcal/mol

T = C, Si, Ge & Sn

n = 0	0.9 kcal/mol
n = 1*	6 - 9 kcal/mol
SnF ₄	25.5 kcal/mol

Tetrel-bonding?



Advances in Inorganic Chemistry and

Radiochemistry

Volume 15, 1972, Pages 1-58

Secondary Bonding to Nonmetallic Elements

N.W. Alcock

Show more

[https://doi.org/10.1016/S0065-2792\(08\)50016-3](https://doi.org/10.1016/S0065-2792(08)50016-3)

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Tetrel-bonding?

Biological systems

Supramolecular association in crystals -
holding molecules together
moderation by steric effects
influence upon coordination geometry

Energies of stabilisation comparable to (HB)²

Well documented in the literature -
Secondary-Bonding

Gold Chemistry

Competition between

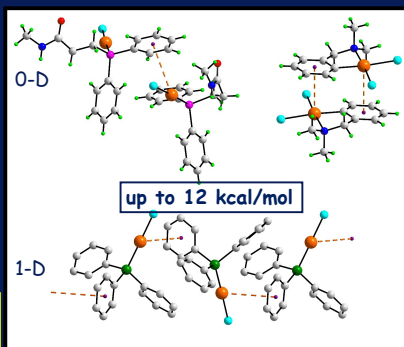
i) Au...Au and hydrogen-bonding



Comparable in energy to HB

Schmidbaur, *Nature* **413** (2001) 31.

Intermolecular Au...π(arene) interactions



RSC Advances **5** (2015) 41401.

Gold Chemistry

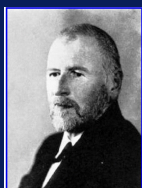
Competition between

i) Au...Au and hydrogen bonding

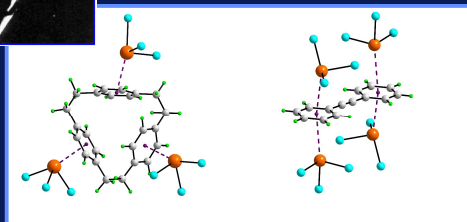
ii) Au...Au and Au...π(arene)

(HB)²: Similar in energy = 5 - 15 kcal/mol

Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



"Menšutkin complexes"



Biology?

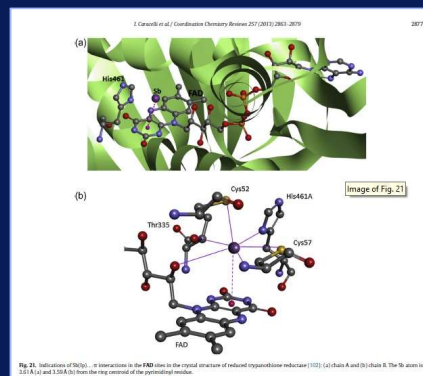


Fig. 21. Indications of $M(lp) \cdots \pi$ interactions in the FAD site in the crystal structure of reduced cytoplasmic reductase (112) (a) (b) (c) (d) (e) (f) (g) (h) (i) (j) (k) (l) (m) (n) (o) (p) (q) (r) (s) (t) (u) (v) (w) (x) (y) (z) (aa) (ab) (ac) (ad) (ae) (af) (ag) (ah) (ai) (aj) (ak) (al) (am) (an) (ao) (ap) (aq) (ar) (as) (at) (au) (av) (aw) (ax) (ay) (az) (ba) (bb) (bc) (bd) (be) (bf) (bg) (bh) (bi) (bj) (bk) (bl) (bm) (bn) (bo) (bp) (bq) (br) (bs) (bt) (bu) (bv) (bw) (bx) (by) (bz) (ca) (cb) (cc) (cd) (ce) (cf) (cg) (ch) (ci) (cj) (ck) (cl) (cm) (cn) (co) (cp) (cq) (cr) (cs) (ct) (cu) (cv) (cw) (cx) (cy) (cz) (da) (db) (dc) (dd) (de) (df) (dg) (dh) (di) (dj) (dk) (dl) (dm) (dn) (do) (dp) (dq) (dr) (ds) (dt) (du) (dv) (dw) (dx) (dy) (dz) (ea) (eb) (ec) (ed) (ee) (ef) (eg) (eh) (ei) (ej) (ek) (el) (em) (en) (eo) (ep) (eq) (er) (es) (et) (eu) (ev) (ew) (ex) (ey) (ez) (fa) (fb) (fc) (fd) (fe) (ff) (fg) (fh) (fi) (fj) (fk) (fl) (fm) (fn) (fo) (fp) (fq) (fr) (fs) (ft) (fu) (fv) (fw) (fx) (fy) (fz) (ga) (gb) (gc) (gd) (ge) (gf) (gg) (gh) (gi) (gj) (gk) (gl) (gm) (gn) (go) (gp) (gq) (gr) (gs) (gt) (gu) (gv) (gw) (gx) (gy) (gz) (ha) (hb) (hc) (hd) (he) (hf) (hg) (hh) (hi) (hj) (hk) (hl) (hm) (hn) (ho) (hp) (hq) (hr) (hs) (ht) (hu) (hv) (hw) (hx) (hy) (hz) (ia) (ib) (ic) (id) (ie) (if) (ig) (ih) (ii) (ij) (ik) (il) (im) (in) (io) (ip) (iq) (ir) (is) (it) (iu) (iv) (iw) (ix) (iy) (iz) (ja) (jb) (jc) (jd) (je) (jf) (jg) (jh) (ji) (jj) (jk) (jl) (jm) (jn) (jo) (jp) (jq) (jr) (js) (jt) (ju) (jv) (jw) (jx) (jy) (jz) (ka) (kb) (kc) (kd) (ke) (kf) (kg) (kh) (ki) (kj) (kk) (kl) (km) (kn) (ko) (kp) (kq) (kr) (ks) (kt) (ku) (kv) (kw) (kx) (ky) (kz) (la) (lb) (lc) (ld) (le) (lf) (lg) (lh) (li) (lj) (lk) (ll) (lm) (ln) (lo) (lp) (lq) (lr) (ls) (lt) (lu) (lv) (lw) (lx) (ly) (lz) (ma) (mb) (mc) (md) (me) (mf) (mg) (mh) (mi) (mj) (mk) (ml) (mn) (mo) (mp) (mq) (mr) (ms) (mt) (mu) (mv) (mw) (mx) (my) (mz) (na) (nb) (nc) (nd) (ne) (nf) (ng) (nh) (ni) (nj) (nk) (nl) (nm) (nn) (no) (np) (nq) (nr) (ns) (nt) (nu) (nv) (nw) (nx) (ny) (nz) (oa) (ob) (oc) (od) (oe) (of) (og) (oh) (oi) (oj) (ok) (ol) (om) (on) (oo) (op) (oq) (or) (os) (ot) (ou) (ov) (ow) (ox) (oy) (oz) (pa) (pb) (pc) (pd) (pe) (pf) (pg) (ph) (pi) (pj) (pk) (pl) (pm) (pn) (po) (pp) (pq) (pr) (ps) (pt) (pu) (pv) (pw) (px) (py) (pz) (qa) (qb) (qc) (qd) (qe) (qf) (qg) (qh) (qi) (qj) (qk) (ql) (qm) (qn) (qo) (qp) (qq) (qr) (qs) (qt) (qu) (qv) (qw) (qx) (qy) (qz) (ra) (rb) (rc) (rd) (re) (rf) (rg) (rh) (ri) (rj) (rk) (rl) (rm) (rn) (ro) (rp) (rq) (rr) (rs) (rt) (ru) (rv) (rw) (rx) (ry) (rz) (sa) (sb) (sc) (sd) (se) (sf) (sg) (sh) (si) (sj) (sk) (sl) (sm) (sn) (so) (sp) (sq) (sr) (ss) (st) (su) (sv) (sw) (sx) (sy) (sz) (ta) (tb) (tc) (td) (te) (tf) (tg) (th) (ti) (tj) (tk) (tl) (tm) (tn) (to) (tp) (tq) (tr) (ts) (tt) (tu) (tv) (tw) (tx) (ty) (tz) (ua) (ub) (uc) (ud) (ue) (uf) (ug) (uh) (ui) (uj) (uk) (ul) (um) (un) (uo) (up) (uq) (ur) (us) (ut) (uu) (uv) (uw) (ux) (uy) (uz) (va) (vb) (vc) (vd) (ve) (vf) (vg) (vh) (vi) (vj) (vk) (vl) (vm) (vn) (vo) (vp) (vq) (vr) (vs) (vt) (vu) (vv) (vw) (vx) (vy) (vz) (wa) (wb) (wc) (wd) (we) (wf) (wg) (wh) (wi) (wj) (wk) (wl) (wm) (wn) (wo) (wp) (wq) (wr) (ws) (wt) (wu) (wv) (ww) (wx) (wy) (wz) (xa) (xb) (xc) (xd) (xe) (xf) (xg) (xh) (xi) (xj) (xk) (xl) (xm) (xn) (xo) (xp) (xq) (xr) (xs) (xt) (xu) (xv) (xw) (xx) (xy) (xz) (ya) (yb) (yc) (yd) (ye) (yf) (yg) (yh) (yi) (yj) (yk) (yl) (ym) (yn) (yo) (yp) (yq) (yr) (ys) (yt) (yu) (yv) (yw) (yx) (yy) (yz) (za) (zb) (zc) (zd) (ze) (zf) (zg) (zh) (zi) (zj) (zk) (zl) (zm) (zn) (zo) (zp) (zq) (zr) (zs) (zt) (zu) (zv) (zw) (zx) (zy) (zz)

Energy?

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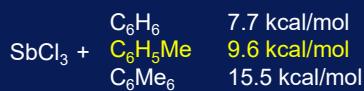
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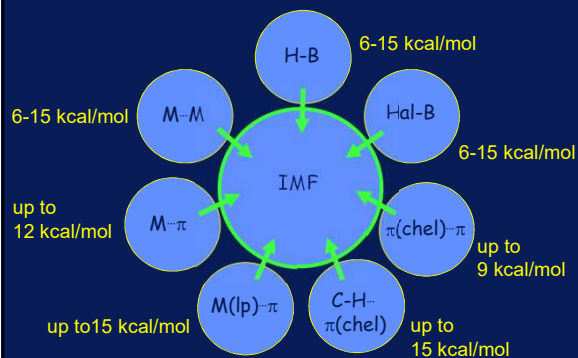
Cite this: Chem. Commun., 2016,
52, 7520.
Received 17th December 2015,
Accepted 27th January 2016
DOI: 10.1039/C5CC03053K

On the nature of the stabilisation of the $E \cdots \pi$
pnictogen bond in the $SbCl_3 \cdots \text{toluene}$ complex†

Rabindranath Lo,^a Petr Švec,^b Zdeňka Růžicková,^b Aleš Růžicka^a and
Pavel Hobza^{a,c}



Overview



Conclusions

More to supramolecular life than $(HB)^2$
"Emerging" interactions are competitive
Global molecular packing

"Egg Causality Dilemma"



Sunway University



Fortuna Eruditis Favet ("Fortune favours the prepared mind")